1.0

1.1

1.25   1.4   1.6

4.5
50
2.8   2.5
3.2   2.2
3.6
4.0   2.0

1.8

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TRANSFORMATION TOUGHENING

PART 3: EXPERIMENTAL OBSERVATIONS IN THE $ZrO_2-Y_2O_3$ SYSTEM

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ABSTRACT

Materials in the $ZrO_2-Y_2O_3$ system (< 7.5 m/o Y_2O_3) were fabricated to investigate the conditions required to retain the metastable, tetragonal phase and to determine the contribution of the stress-induced martensitic reaction to fracture toughness. Retention of the tetragonal phase was optimized by minimizing porosity and maintaining the grain size below a critical valve. The critical grain size increased from 0.2 μm to 1 μm for compositions ranging between 2 m/o Y_2O_3 to 3 m/o Y_2O_3, respectively. These results are consistent with the theories developed regarding the thermodynamics of the martensitic reaction in a constrained state. In the tetragonal plus cubic phase field (compositions between 3.0 and 7.5 m/o Y_2O_3), the critical stress intensity factor decreased from 6.3 $MPa \cdot m^{1/2}$ to 3.0 $MPa \cdot m^{1/2}$ as the volume fraction of the retained, tetragonal phase decreased to zero. Theoretical results, derived from the concept that the crack's stress field does work to unconstrain the transformation, are in good agreement with the experimental results.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Materials in the $ZrO_2-Y_2O_3$ system ($\leq$ 7.5 m/o Y_2O_3) were fabricated to investigate the conditions required to retain the metastable, tetragonal phase and to determine the contribution of the stress-induced martensitic reaction to fracture toughness. Retention of the tetragonal phase was optimized by minimizing porosity and maintaining the grain size below a critical valve. The critical grain size increased from 0.2 μm to 1 μm for compositions ranging between 2 m/o Y_2O_3 to 3 m/o Y_2O_3, respectively. These results are consistent with the theories developed regarding the thermodynamics of the

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martensitic reaction in a constrained state. In the tetragonal plus cubic phase field (compositions between 3.0 and 7.5 m/o Y_2O_3), the critical stress intensity factor decreased from 6.3 MPa·m$^{1/2}$ to 3.0 MP·a$^{1/2}$ as the volume fraction of the retained, tetragonal phase decreased to zero. Theoretical results, derived from the concept that the crack's stress field does work to unconstrain the transformation, are in good agreement with the experimental results.

Introduction

The first part[1] of this series presented a thermodynamic analysis to explain the size effect associated with a constrained phase transformation. It was shown that a critical inclusion (or grain) size exists, below which the constrained transformation is thermodynamically unfavorable. The size effect arises from surface phenomena associated with the transformation, viz. twinning and/or microcracking, which relieve constraint. These surface phenomena can be avoided when the material is fabricated with an inclusion size less than the critical size. It was further shown that the critical size could be increased by either increasing the elastic modulus of the constraining matrix or alloying to lower the chemical free energy change associated with the transformation. From a practical viewpoint, increasing the critical size can relax the constraints imposed on the fabricator who must contend with inclusion coursening and grain growth during heat treatment and/or sintering.

In Part 2,[2] the contribution of the constrained inclusions to the fracture toughness was analyzed. It was shown that the energy absorbed in the fracture process was equivalent to the work performed by the loading system to stress-induce the transformation. The contribution of the stress-induced transformation was thus shown to be related to the chemical free energy change associated with the transformation, the volume of material that remains in the transformed state during crack extension and the elastic modulus of the composite.
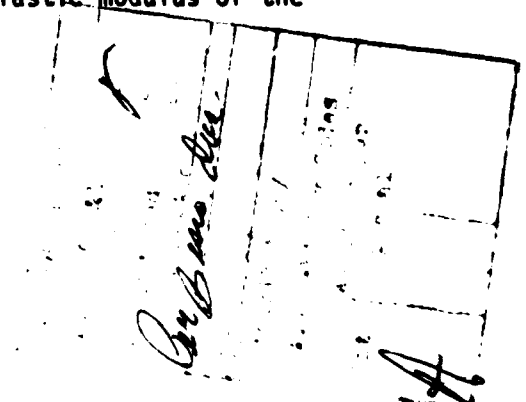
The present part reports the experimental work with materials in the ZrO_2-Y_2O_3 system and is concerned with both retention of the high temperature tetragonal structure of ZrO_2 and its effect on fracture toughness. Figure 1 illustrates[3,4] that Y_2O_3 forms a solid solution with ZrO_2 and lowers the tetragonal → monoclinic transformation temperature from ~ 1200°C to ~ 565°C at a Y_2O_3 content of ~ 3.5 mole %. Thus, effects concerned with changing the chemical free energy could be studied with Y_2O_3 additions up to ~ 3.5 m/o. Figure 1 also shows a two phase, tetragonal + cubic, field exists between ~ 3.5 m/o Y_2O_3 and ~ 7 m/o Y_2O_3, in which a two-phase material could be fabricated to determine the effect of the tetragonal phase content on fracure toughness. The ZrO_2-Y_2O_3 system appeared to be useful in obtaining data that may support some of the theoretical predictions made in Parts 1 and 2. In addition, Gupta et al,[5] have already demonstrated that single phase, tetragonal ZrO_2 could be fabricated in this system. Experimental effort was thus concentrated in three areas: 1) effect of density on retention of the tetragonal phase, 2) the critical grain size required for phase retention, and 3) the fracture toughness as related to composition.

3.   Experimental Procedures

Composite powders (0 - 7.5 m/o Y_2O_3) were prepared by mixing in a mortar and pestal submicron size ZrO_2 powder* with the appropriate amount of yttrium nitrate in methanol, after determining the conversion factor for the
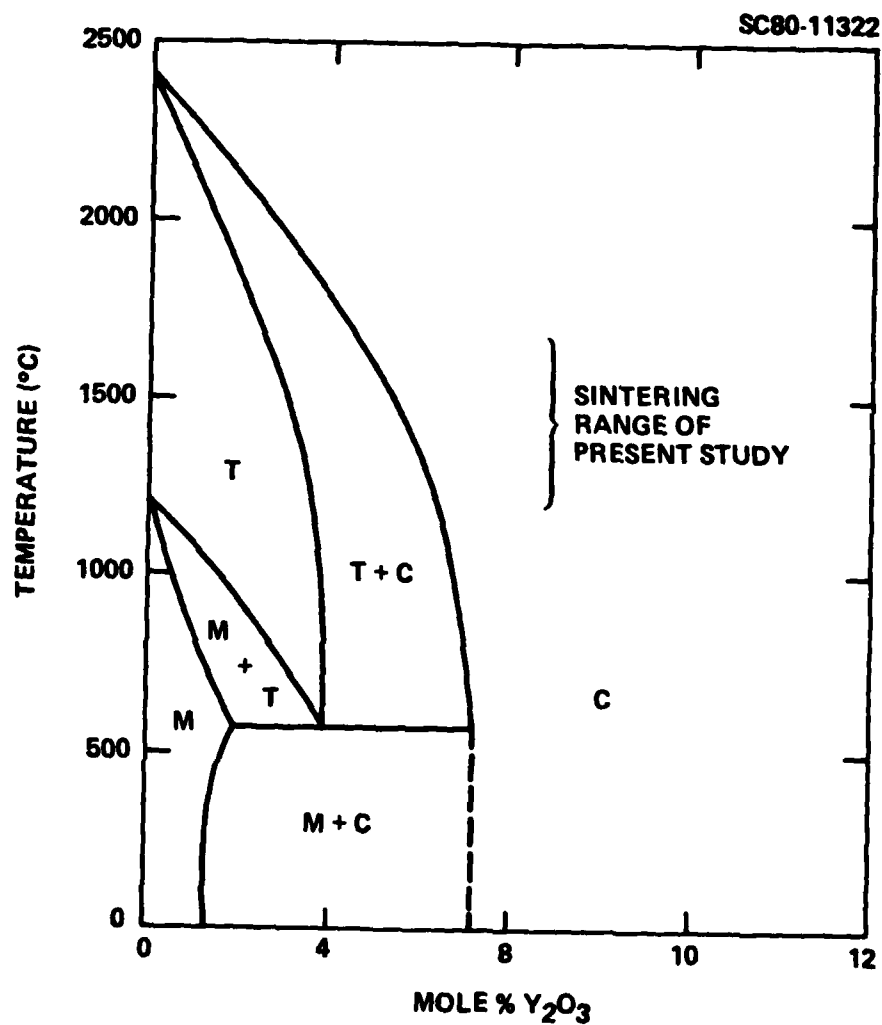
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*Zicar Corp., Florida, N.Y.

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Fig. 1   The portion of the ZrO_2-Y_2O_3 system used in the present work.[3,4]

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decomposition of yttrium nitrate to Y_2O_3. Prior to cold pressing and sintering, the composite powders were calcined for 4 hrs at 400°C. Sintering experiments were performed in an air environment at temperatures between 900° and 1650°C. After sintering, densities[*] were obtained by either dimensional/weight measurements or a water displacement technique. X-ray diffraction was used for phase identification. Monoclinic and tetragonal phase contents were determined from their relative intensity ratios of their respective ($1\bar{1}1$) and (111) diffraction peaks by using a planometer. The presence of the cubic phase was determined by both the (311) and the (400) diffraction peaks which would split the respective diffraction peaks of the tetragonal phase.

For selected materials the critical stress intensity factor, K_c, was determined at room temperatures by using the indentation technique developed by Evans and Charles.[6] Prior to using this technique, the surface of each specimen was finely polished and x-rayed to ensure that the surface was not noticeably altered by the preparation procedure. It should be noted that rough grinding will induce the tetragonal → monoclinic transformation at the surface, and the damaged layer can be removed (within current detectability limits of ~ 0.5 μm)[7] by polishing. The intercept method was used to determine grain size on SEM micrographs of fracture surfaces.

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[*]The theoretical density of ZrO_2/Y_2O_3 materials were calculated from Scott's[4] lattice parameter data.

3.   Results and Discussion

3.1   General Fabrication Observations

Approximately 80% of the total shrinkage occurred rapidly (< 2 hrs) between 1150° and 1250°C; further shrinkage required temperatures > 1350°C. Densities of 82% to 87% theoretical could be achieved at 1200°C/24 hrs. For compositions containing < 6 m/o Y_2O_3, densities of 88% to 93% theoretical could be achieved by sintering 24 hrs at 1200°C followed by 2 hrs at 1400°C. Compositions containing > 6 m/o Y_2O_3 required an additional 2 hrs at 1550°C.

3.2   Retention of Tetragonal ZrO_2: Effect of Density

Composite powders containing 2.5 m/o Y_2O_3 were uniaxial cold pressed at different stresses to achieve different grain densities and then were sintered together for 2 hrs at 1500°C. Figure 2 plots the results of this experiment in terms of the % retained tetragonal phase vs the % of theoretical density achieved during sintering. It can be concluded that the retention of the high temperature tetragonal phase at room temperature depends on the density achieved during fabrication. This conclusion shows that phase retention is directly related to the constraint imposed by neighboring grains on one another. Porosity lowers the elastic modulus and introduces free surface. The effect of both of these factors would reduce the strain energy associated with the transformation allowing larger grains and/or grains bounded by more free surface than neighboring grains to undergo the transformation during cooling.[1]
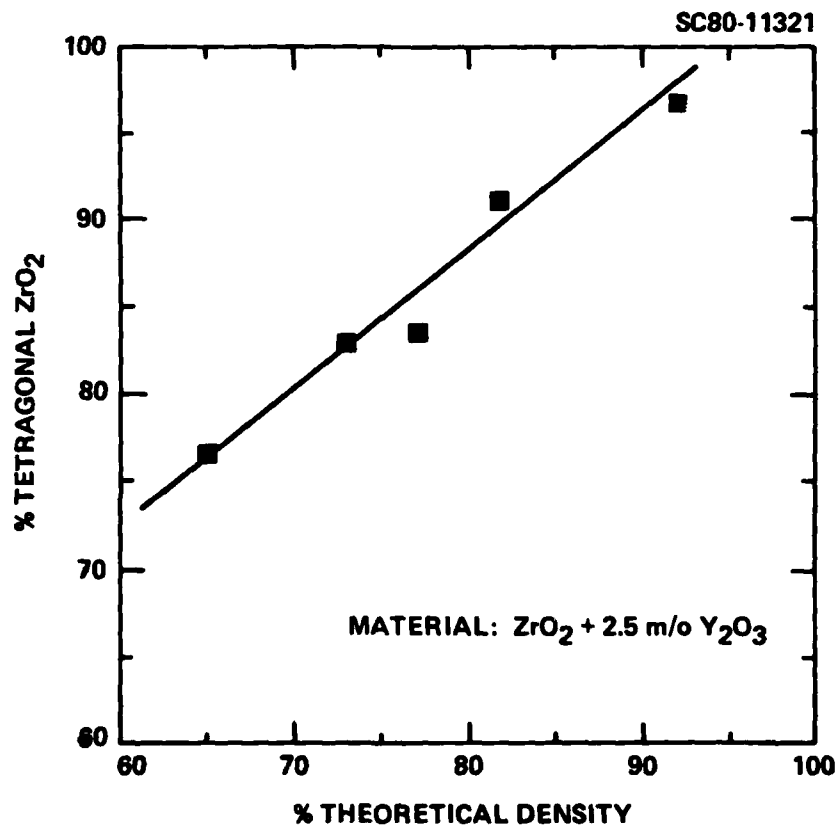
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Fig. 2   The effect of density on retention of tetragonal ZrO_2 + 2.5 m/o Y_2O_3.

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3.3 Retention of Tetragonal ZrO$_2$: Critical Grain Size

Composite powders containing 0, 1.5, 2.0, 2.5, 3.0 and 3.5 m/o Y$_2$O$_3$ were cold pressed and sintered for 2 hrs at temperatures ranging from 1200° to 1600°C. Detailed grain size measurements were made on the 2.0 m/o Y$_2$O$_3$ composition as a function of temperature; these results are shown in Fig. 3. Measurements on other selected compositions were in agreement with these data. The phase content of each specimen was compared to the grain size measurement in order to determine the critical grain size required to retain > 90% of the tetragonal phase. Since densities between 80% and 90% of theoretical could only be achieved with the sintering conditions stated, monoclinic contents < 10% were neglected. (If full density could be achieved, the critical grainsize would be expected[1] to be somewhat smaller than those reported in Fig. 4.)

As shown in Fig. 4, a high tetragonal content could not be achieved for the composition containing 1.5 m/o Y$_2$O$_3$, i.e., grain growth during sintering pre-cluded an average grain size < 0.2 μm. The pure ZrO$_2$ was completely monoclinic under all conditions. More important, Fig. 4 shows that the average critical grain size significantly increases beween 2 and 3 m/o Y$_2$O$_3$. The composition containing 3.5 m/o Y$_2$O$_3$ contained a detectable amount of cubic phase, indicating that it lies in the tetragonal + cubic phase field at temperatures > 1200°C (see Fig. 1).

The increase in the critical grain size with increasing Y$_2$O$_3$ content is consistent with the theortical prediction that the critical grain size would increase as the magnitude of the change in chemical free energy decreases (see Part 1).
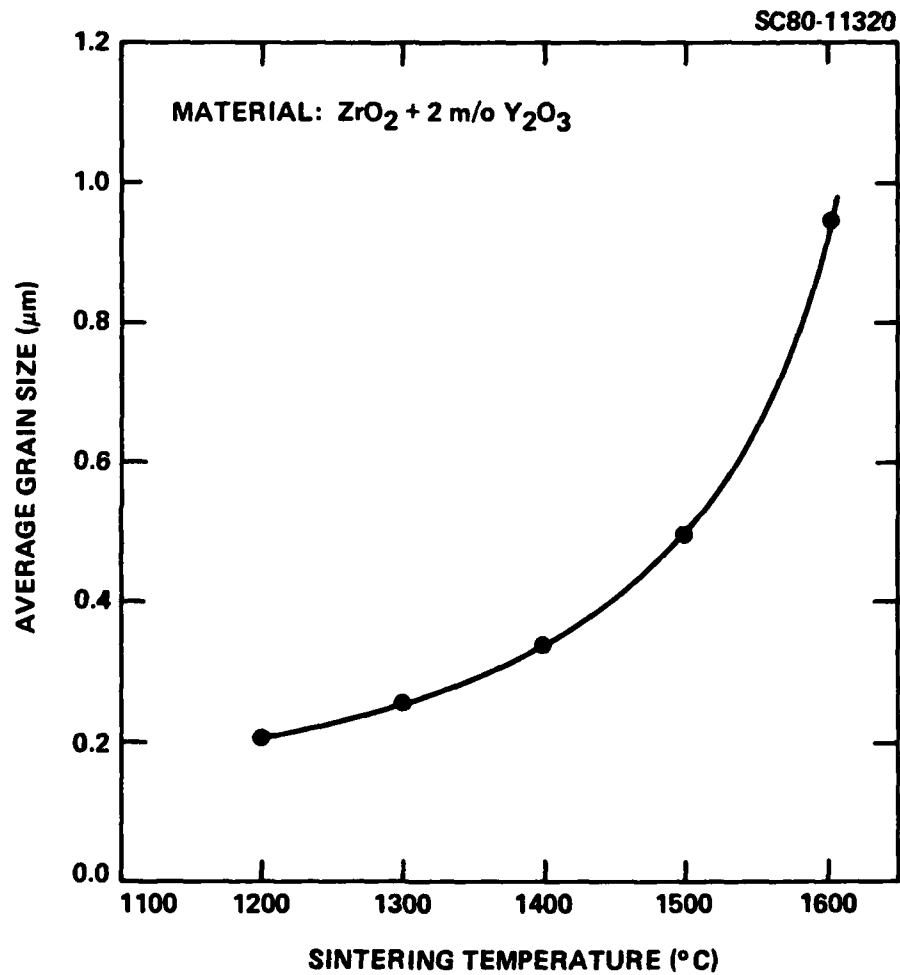
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Fig. 3   Average grain size vs sintering temperature determined for the ZrO_2 material containing 2 m/o Y_2O_3.

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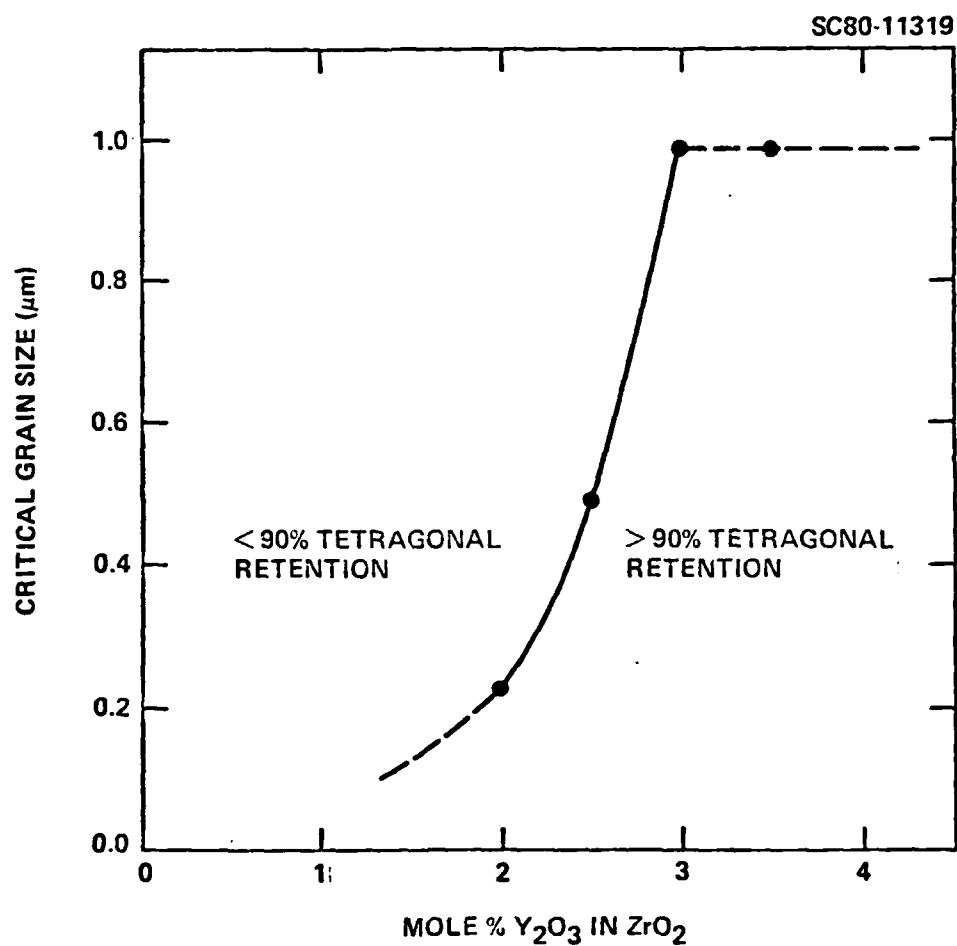

Fig. 4   Critical grain size vs Y_2O_3 content in tetragonal ZrO_2.

3.4　Fracture Toughness

The object of this task was to measure fracture toughness as a function of the retained tetragonal phase. Composite powders containing 1.5 to 7.5 m/o Y_2O_3 in increments of 0.5 m/o Y_2O_3 were prepared. According to Fig. 1, compositions with > 3 m/o Y_2O_3 should contain increasing contents of the cubic phase. Sintering schedules were optimized (see Section 3.1) to produce materials with a density in the range of 88% to 93% of theoretical. Phase identification results were consistent with the concepts required for retention of the tetragonal phase and the phase diagram for this system (Fig. 1). A two phase, tetragonal + cubic, material was produced between 3 m/o Y_2O_3 and 7 m/o Y_2O_3; the volume fraction of the tetragonal phase decreased from one at 3.0 m/o Y_2O_3 to zero at 7.0 m/o Y_2O_3. Only the 1.5 m/o Y_2O_3 composition contained an appreciable amount (> 10%) of the monoclinic phase, because the average grain size was in excess of the critical value. The monoclinic phase was not detected in compositions containing > 3 m/o Y_2O_3.

Results of the stress intensity factor measurements are shown in Fig. 5 as a function of the Y_2O_3 content and the volume content of the tetragonal phase. Three indentations were used to determine K_c for each composition; data scatter illustrates high and low values. This figure shows that K_c drops from 6.3 MPa·$m^{1/2}$ to 3.0 MPa·$m^{1/2}$ as the volume fraction of the tetragonal phase decreases to zero. The 1.5 m/o Y_2O_3 composition had a relatively low K_c due, apparently, to the large amount of monoclinic phase.

The solid line in Fig. 5 was obtained from the calculated effect of the tetragonal volume fraction on K_c by using[2]
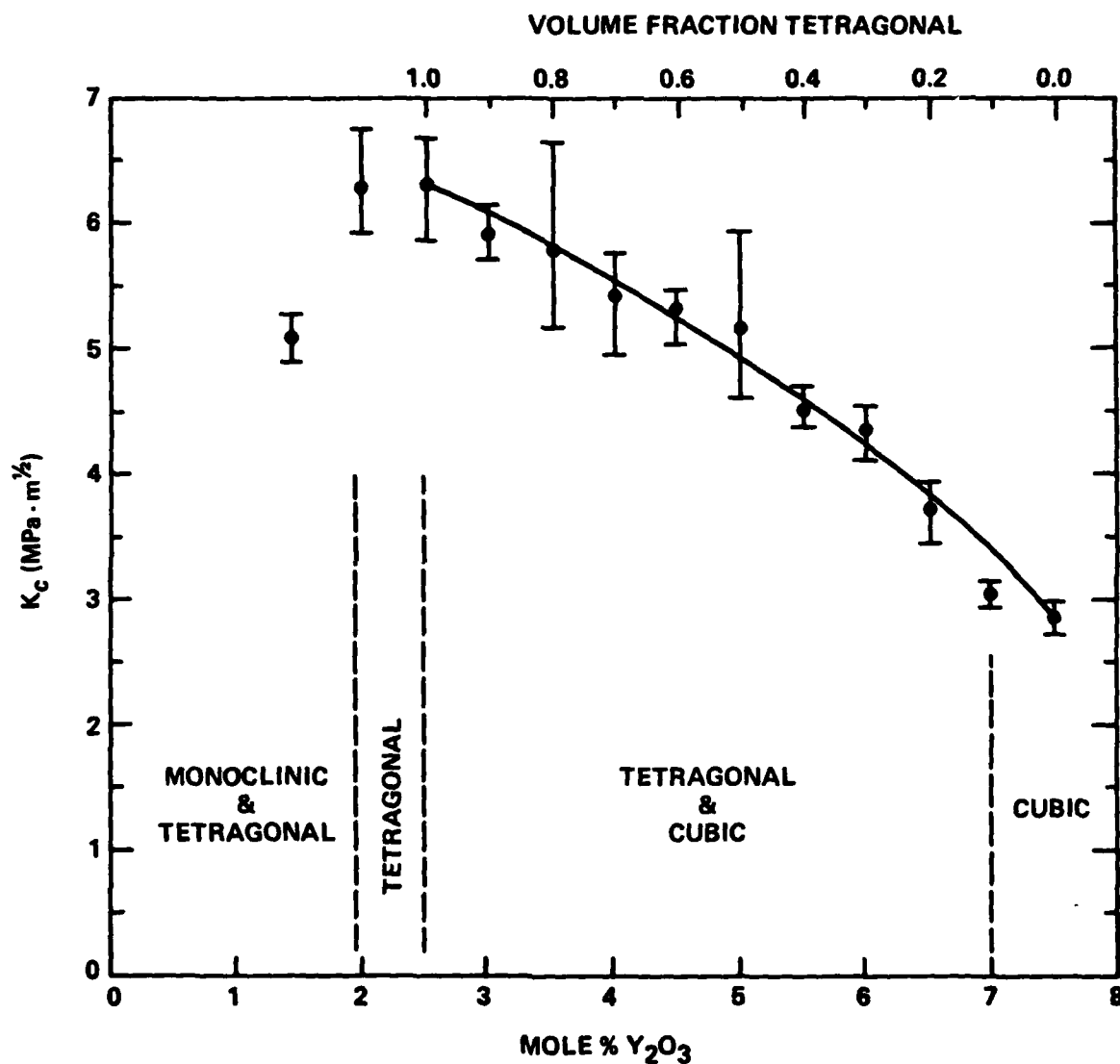
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Fig. 5   Fracture toughness (K_c) vs mole % of Y_2O_3 in ZrO_2.

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$$K_c = \left[K_0^2 + \frac{2(|\Delta G^c| - \Delta U_{se}f) E_c V_i R}{(1 - \nu_c^2)} \right]^{1/2} \quad , \tag{1}$$

where:

K_0 = the fracture toughness of the cubic phase (3.0 MPa·m$^{1/2}$),

$|\Delta G^c|$ = the magnitude of the chemical free energy change associated with the transformation,

$\Delta U_{se}f$ = the residual strain energy associated with the transformed grains near the fracture surface

E_c, ν_c = the elastic modulus and Poisson's ratio of the composite,

R = the depth of the transformation zone from the fracture surface, and

V_i = the volume fraction of the tetragonal phase.

Equation (1) can be rewritten as

$$K_c^2 - K_0^2 = C V_i \quad , \tag{2}$$

where C can be evaluated where $V_i = 1.0$ to predict the effect of volume fraction. As shown, the predicted effect of the tetragonal volume fraction on K_c is in perfect agreement with the experimental values.

By assuming that the depth of the transformation zone is approximately equivalent to the grain size,[2] one can use Eq. (1), the experimental values of K_c and K_0, and the expected elastic properties of the material to determine the fac-

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tor ($|\Delta G^C| - \Delta U_{se}f$). This factor is the work per unit volume loss during the stress induced transformation.[2] Using the values E_c = 165 GPa*, ν_c = 0.25 and R = 0.5 μm, the work done per unit volume of transformed material was calculated as 176 MJ/m^3.

3.5 Fractography

Figure 6 illustrates the typical fracture surface topography of four compositions (2 m/o Y_2O_3, major: monoclinic, minor: tetragonal; 3.5 m/o Y_2O_3, major: tetragonal, trace: cubic; 7.5 m/o Y_2O_3, major: cubic; 5 m/o Y_2O_3, major: cubic, minor: tetragonal; all ~ 85% dense), sintered at 1600°C for 2 hrs. Inter- granular fracture (Fig. 6a) was typical of the high monoclinic materials, sugges- ting that the crack path followed the intergranular microcracks produced during fabrication as a result of the phase transformation. Such materials were quite friable. Irregular, transgranular fracture was typical of tetragonal materials (Fig. 6b). The irregular fracture topography of individual grains may be a re- sult of the cracks interacting with the complex internal structure of the twinned monoclinic grains. Fig. 6b also indicates that intergranular microcracks <u>were</u> <u>not</u> produced ahead of the crack front, because of the stress-induced transforma- tion, i.e., if microcracks were present, the fracture surface would resemble that shown in Fig. 6a. A smooth transgranular fracture surface was typical for the cubic materials (Fig. 6c). The porosity (~ 15%) associated with these materials is easily recognized in the cubic material because of the near planar topography

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*The elastic modulus of dense $ZrO_2(t)$ is 207 GPa,[8] the value of 165 GPa was calculated for a material with 10% porosity.

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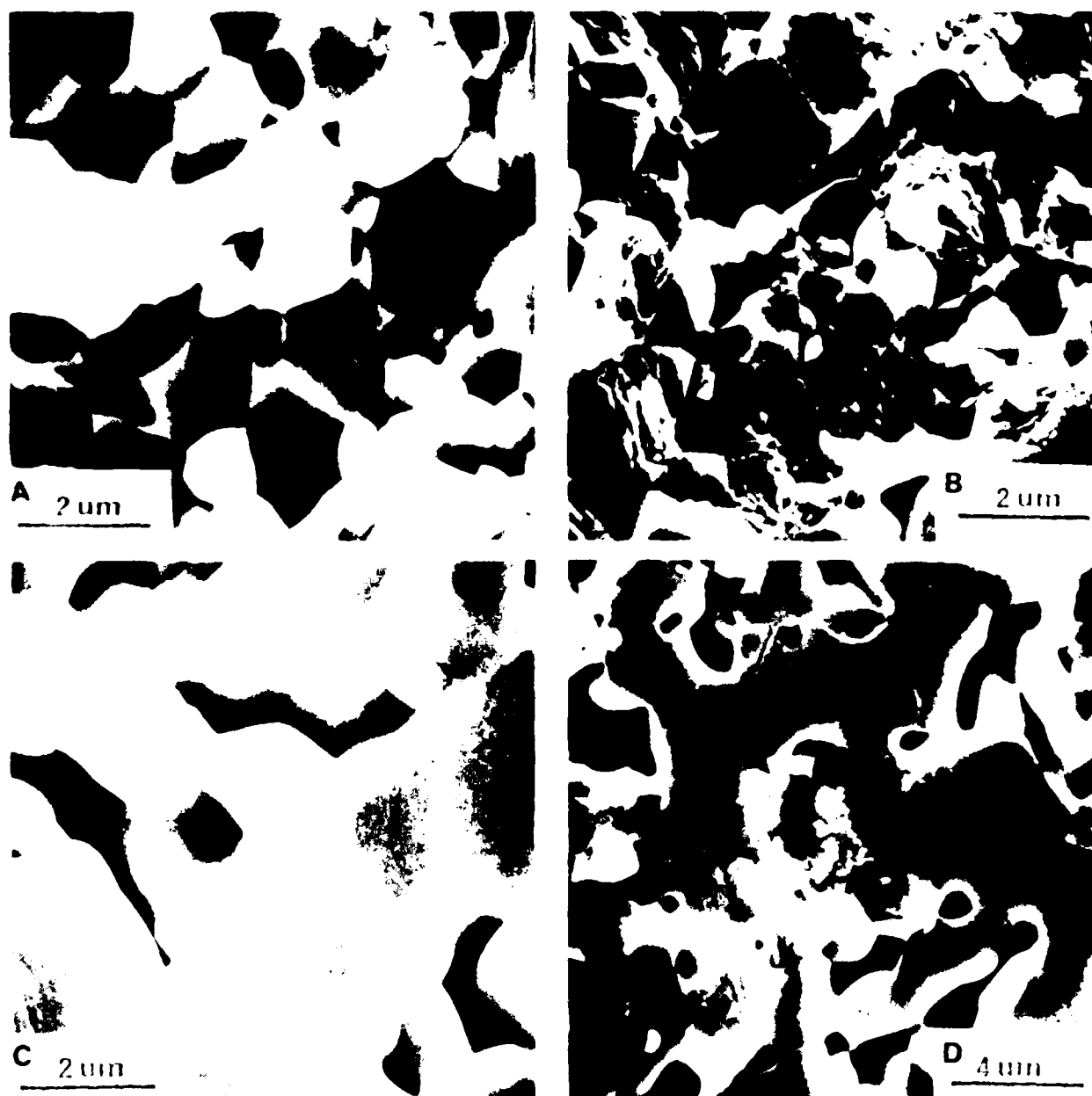Fig. 6   Fracture surfaces of a) monoclinic ZrO_2 + 2 m/o Y_2O_3 composition,
b) tetragonal ZrO_2 + 3.5 m/o Y_2O_3 composition, c) cubic ZrO_2 + 7.5 m/o
Y_2O_3, and d) mixed tetragonal + cubic ZrO_2 + 5 m/o Y_2O_3. All sintered
at 1600°C/2 hrs.

of the fracture surface. Since both the tetragonal and cubic phases produce different fracture topographies, it was relatively easy to recognize tetragonal grains surrounded by cubic grains for two phase compositions such as the 5 m/o Y_2O_3 composition shown in Fig. 6d. This observation suggests that the two phases in such compositions (3 m/o < Y_2O_3 < 6.5 m/o) are present as separate grains, instead of tetragonal precipitates within a cubic matrix as produced by fabricating in the cubic phase field and quenching into the tetragonal + cubic phase field.[9]

4. Conclusions

Retention of the tetragonal phase was found to depend on both density and grain size. The dependence on density is consistent with the need for self-constraint and with the concepts developed regarding the thermodynamics of the martensitic reaction in an elastically constrained matrix. The effect of Y_2O_3 on the critical grain size is consistent with the theory relating the chemical free energy change to the size effect produced by surface phenomena (e.g., twinning and microcracking) that can accompany the transformation.

The contribution of the stress-induced transformation to the fracture toughness is significant and is directly related to the volume fraction of the retained tetragonal phase. Theory developed to explain this contribution is in good agreement with experimental data validating the concept that the transformation's contribution lies with the work done to unconstrain the martensitic reaction. Fractography indirectly supports this concept.

Acknowledgement

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